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ANTICORROSIVE COPPER ALLOY FOR OCEAN USE

[海洋用耐食銅合金]

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APPLICANT(S)	(71):	MITSUI MINING & SMELTING CO., LTD.
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FOREIGN TITLE	[54A]:	海洋用耐食銅合金

SPECIFICATION

1. Title of the Invention

Anticorrosive Copper Alloy for Ocean Use

2. Scope of Patent Claims

(1) An anticorrosive copper alloy for ocean use, comprising of 20 to 37% by weight of Zn, 0.05 to 0.5% by weight of Al, 0.05 to 0.4% by weight of Sn, 0.01 to 0.05% by weight of P, the remaining parts of copper, and unavoidable impurities, which is a characteristic of the restraining dezincification phenomenon.

(2) An anticorrosive copper alloy for ocean use, comprising of 20 to 37% by weight of Zn, 0.05 to 0.5% by weight of Al, 0.05 to 0.4% by weight of Sn, 0.01 to 0.05% by weight of P, 0.05 to 0.5% by weight of Ni, the remaining parts of copper, and unavoidable impurities, which is a characteristic of the restraining dezincification phenomenon.

3. Detailed Description of the Invention

[Industrial Application Field]

The present invention relates to an anticorrosive copper alloy, which is used for a wire net for a fish pen, a lattice for a sluice gate, a cover for a steel stake, and the like, in an ocean environment and has both properties for anti-algae and dezincification.

[Prior Art]

Generally, anticorrosive metal materials, used in the ocean or a situation contacting a tidal zone, demand functions such as a strength to correspond to individual uses, as well as organisms sticking less, such as shellfish and algae (hereafter, referred to as antialgal properties).

To secure the antialgal properties, a method to apply coating materials containing tin compounds has been conventionally known. Recently, nickel silver, as typified in 90 Cu - 10 Ni alloy, tends to be used as materials for a fish pen, a lattice for a sluice gate, and the like. This method utilizes an action that can avoid attaching organisms, such as shellfish and algae, due to the influence of Cu ions that liquate out into seawater.

However, the former method to coat coating materials containing tin compounds cannot avoid the problems of the coating materials, such as deterioration, longevity, and poor construction, and thus is hardly expected to have a long life. In contrast, nickel silver is superior in both antialgal and anticorrosive properties but has a defect that is, an anticorrosive membrane is getting thicker in a several years, the quantity of liquation of Cu ions decreases, and thus algae easily attach. Moreover, the price of bullion is high, and thus the use of nickel silver is limited.

On the contrary, if brass, which costs cheaper, is used in the ocean, it shows superior antialgal properties but causes dezincification corrosion. Thus its strength lowers over time, and it will be unsuitable for use. Accordingly, development of an anticorrosive alloy for ocean use has been desired.

[Objective of the Invention]

The objective of the present invention is to provide an anticorrosive copper alloy for ocean use, which prevents the dezincification corrosion that brass causes as mentioned above, secures a long-term liquation of copper ions, has antialgal properties, and is superior in both general anticorrosion and strength.

[Problems to Be Solved by the Invention]

The present invention was completed to achieve the above-mentioned objective. For embodiment, when a copper alloy is used for creating a wire net for a fish pen, the desirable characteristics are as follows:

(1) Copper ions liquate from materials for a fish pen for a long time in order to secure the antialgal properties.

(2) When the liquation of copper ions is secured, make sure that the quantity of liquation does not become too much. That is, its life becomes short due to

insufficient anti-corrosivity.

(3) Selective leaching phenomenon, such as dezincification corrosion, is not caused.

(4) The strength is so high as to endure a typhoon and the like, and thinning is capable.

(5) Its process-ability is good.

(6) Local corrosion hardly occurs.

(7) Its ingredients are cheap.

[Means to Solve the Problems]

The present inventors have eagerly studied the relationships between ingredients of an anticorrosive alloy for ocean use and the aforementioned desirable ingredients and thus obtained the following knowledge to complete the invention. First, Zn is effective to raise the strength of alloy and to lower the prices of the raw materials. When Zn is added, the quantity of liquation of the copper ions gradually decreases but not so much as to exert a baneful influence and is rather favorable. However, since adding Zn causes dezincification corrosion, a countermeasure is necessary. That is, if Zn is less than 20% by weight, the above-mentioned advantage is not obtained sufficiently; if it is more than 37% by weight, the process-ability of alloy decreases, and dezincification corrosion becomes considerable.

Al has actions to raise the strength of the alloy, to restrain the liquation of copper due to the addition of Sn and P, and to secure the anti-corrosivity. If Al is less than 0.05% by weight, this effect is insufficient; if it is more than 0.5% by weight, strong membrane is easily caused on the surface of alloy, the quantity of liquation of copper ions extremely decreases while the time passes, faults are caused in antialgal properties, and the quantity of dezincification corrosion increases.

Sn is effective in restraining dezincification corrosion. If Sn is less than 0.05% by weight, this effect is insufficient; if it is more than 0.4% by weight, its effect is saturated, and its process-ability is damaged simultaneously.

Incidentally, Sn and P are effective in restraining dezincification corrosion respectively and show a multiplier effect to restrain dezincification corrosion when both of them are added.

Ni is effective in miniaturizing crystallized grains to enhance anti-corrosivity, as well as strength. Accordingly, when Ni is also added to the above-mentioned composition of alloy, Ni will further enhance the effects of the present invention. When the amount of Ni contained in the present invention was less than 0.05% by weight, this effect was few; if it was more than 0.5% by weight, dezincification corrosion was easily caused.

As mentioned above, the first anticorrosive copper alloy for ocean use as in the present invention comprises of 20 to 37% by weight of Zn, 0.05 to 0.5% by weight of Al, 0.05 to 0.4% by weight of Sn, 0.01 to 0.05% by weight of P, the remaining parts of copper, and unavoidable impurities. The second alloy comprises of the compositions of Zn, Al, Sn, and P as the ingredients in the first alloy, 0.05 to 0.5% by weight of Ni, the remaining parts of copper and unavoidable impurities and has a characteristic to potentially restrain the dezincification phenomenon.

The effects of the copper alloy by the present invention are described below on the basis of embodiments, also referring to comparison embodiments.

[Embodiments]

Copper alloys, which Table 1 shows, in graphite melting pots respectively were melted in a high-frequency melting furnace and were casted in metal moulds respectively. The lumps of ingot prepared were face-grinded and were repeatedly annealed and rolled until flat materials with the thickness of 1 mm at the finish, equivalent to half H materials wherein the rolling ratio was between 15% and 20%, were produced. The following experiments were conducted with these flat materials.

① The samples were attached to a rotating substance of a water wheel rotated by a speed of 2 m/s in natural seawater

and were left alone for 1,000 hours. The amount of corrosion was calculated with the differences between the weights of samples before and after the test, and was expressed with a unit of mg/day/dm^2.

② As a dezincification test, the samples were soaked in a solution of $CuCl_2$-$2H_2O$ (12.8 g/l) at 75 C on the basis of ISO standards for one day, and then the depth of corrosion at 10 spots on the sections of samples was found. The maximum values of depth were expressed in µm.

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③ 200 mm × 100 mm of test pieces were soaked in seawater for practical use at a depth of 70 cm for one year, and the situation where organisms attached was observed.

④ A tension test was conducted to measure the tensile strength and extension.

Table 1 shows these results below.

Table 1

	Sample No.	Composition of Alloy					Amount of Corrosion (mdd)	Amount of Dezincification (µm)	Antialgal Properties (Note)	Tensile Strength (Kgf/mm^2)	Extension (%)
		Zn	P	Sn	Al	Ni					
Embodiment	1	34	0.03	0.22	0.08	0.09	480	75	○	55	16
Embodiment	2	34	0.04	0.22	.028	0.09	380	100	○	58	14
Embodiment	3	34	0.03	0.22	0.27	--	400	100	○	56	15
Embodiment	4	25	0.01	0.05	0.10	--	270	60	○	50	17
Embodiment	5	35	0.04	0.32	.038	--	240	110	○□	57	14
Comparative Example	6	30	--	--	--	--	250	440	○	46	35
Comparative Example	7	35	0.02	0.21	--	0.19	490	0	○	60	11
Comparative Example	8	32	0.04	0.22	0.59	0.10	180	150	×	62	9

Comparative Example	9	33 0.04 0.21 0.30 0.60	360	640	○	61	8

Note) The antialgal properties are expressed with ○: no organisms attached; ×: barnacles, ascidians, and the like covered more than a half of the surface, and △: a few organisms attached.

As Table 1 shows, the amount of corrosion increases under the existence of Sn and P that were added to prevent dezincification corrosion but also tends to decrease due to the addition of Al. Moreover, the amount of dezincification becomes 0 conversely due to Sn and P as Comparative Example 7 shows but increases a little due to the addition of Al. Furthermore, great amounts of additions of Al and Ni result in dezincification. While the amount of addition of Al increases, the antialgal properties decrease. For the tensile strength and extension, other alloys that have more ingredients added than Comparative Example 6 tend to show high strength and low extension, as well as show the effects of Al, Ni, and Zn.

In addition, the relationships between the amount of corrosion and that of dezincification, which were affected when Al was added to an alloy comprising of 34 to 35 of Cu, 0.02 to 0.04 of Zn, 0.21 to 0.22 of P, and Sn (and Ni), were plotted in Fig. 1 on the basis of the data of Table 1.

As Fig. 1 clearly shows, the alloy as the present invention restrains dezincification, as well as the amount of corrosion.

As Table 1 clearly shows, the alloy as the present invention prevents organisms, such as shellfish and algae, from attaching, due to liquation of Cu ions, increases the mechanical strength of brass to augment the reliability in strength, and can make a wire diameter narrow to decrease materials to be used and thus to further enhance the economical efficiency potentially.

[Effects of the Invention]

As Embodiments clearly show, the anticorrosive copper alloy as the present invention utilizes both superior properties for anticorrosion and anti-alga and is suitable as material for a lattice for sluice gate, a fish pen, a cover for steel stake, outer deck boards of shipping, and the like in the ocean environment or for devices to deal with seawater for use to avoid attaching organisms.

4. Brief Descriptions of the Drawings

Fig. 1 is a graph, which shows both the decreased amount of corrosion and depth of amount of dezincification when Al was added to the present alloy and the like.

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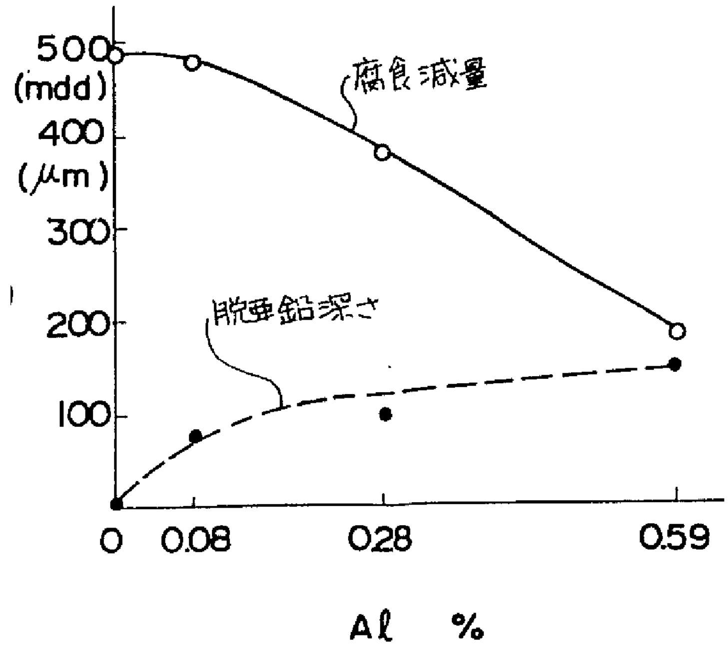
Fig. 1

Decreased Amount of Corrosion (mdd)

Depth of Dezincification (μm)



Amendment (Spontaneous)

To: Commissioner of the Patent Office

September 10, 1984 (Showa 59)

1. Description of the Present Case

    Patent Application No. 59-168764

2. Title of the Invention

    Anticorrosive Copper Alloy for Ocean Use

3. Person making Amendment

    Relationship to the Case: Patent Applicant

    Title (Name): (618) Mitsui Mining & Smelting Co., Ltd.

4. Representative

    Address: Shuwa Dai 2 Toranomon Building

    21-19 1-Chome Toranomon, Minato Ward, Tokyo

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Name: Attorney (6073) Saburo Kimura

5. Date of ( ): Year Month Day

(Sent on: Year Month Day)

6. Objects for the Amendment

Column of "Detailed Description of the Invention" in the Specification

7. Contents of the Amendment

(1) Amend the "due to addition of Sn and P" on line 17, page 4 of the Specification to "caused from addition of Sn and P".

(2) Amend "Incidentally, Sn and P are ... show ..." on lines 7 to 9, page 5 of the Specification to "P is effective to restrain dezincification corrosion; if it is less than 0.01%, the effect is insufficient; if it is more than 0.05%, the effect is saturated, as well as the process-ability becomes poor simultaneously.

Incidentally, Sn and P show a multiplier effect to restrain dezincification corrosion when both of them are added".

(3) Amend "of water wheel" on line 13, page 6 of the Specification to "like a water wheel".

(4) Amend "75 C" on line 17, page 6 of the Specification to "75°C".

(5) Amend the values in the columns of “Amount of corrosion (mdd)” on Table 1 on page 8 of the Specification respectively as follows:

“480” → “48”

“380” → “38”

“400” → “40”

“270” → “27”

“240” → “24”

“250” → “25”

“490” → “49”

“180” → “18”

“360” → “36”